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METHOD FOR MANUFACTURING CONTINUOUS FOAMED BODY OF ETHYLENE
POLYMER OR COPOLYMER

METHOD FOR MANUFACTURING

Yuzuru Ichii et al.

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METHOD FOR MANUFACTURING CONTINUOUS FOAMED BODY OF ETHYLENE
POLYMER OR COPOLYMER

[Echiren jugotai matawa kyojugotai no renzoku kihotai no seiho]

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| Inventors: | Yuzuru Ichii et al. |
| Applicants: | Sumitomo Chemical Co., Ltd. Ichii K.K. Takeyasu Taneike |

[There are no amendments to this patent.]

Claim

A method for manufacturing a continuous foamed body of an ethylene polymer or copolymer, characterized by consisting of a process that heats a compound in which an ethylene polymer or copolymer is mixed with a mixture of a foaming agent, a crosslinking agent with a decomposition temperature of 155°C or lower and a crosslinking agent with a decomposition temperature of 165°C or higher for a fixed time and generates a crosslinked first intermediate product with a decomposition rate of 60% or less of the mixed foaming agent; a process that heats the first intermediate product to a temperature higher than that of the first process and generates a second intermediate product having easily breakable independent foams by

decomposing the remaining foaming agent and crosslinking agent; and a third process that breaks the independent foams by compressing the second intermediate product.

Detailed explanation of the invention

The present invention pertains to a method for manufacturing a continuous foamed body of an industrially applicable ethylene polymer or copolymer.

As a method for manufacturing a foamed body having a continuous foam, a method that breaks a foam film by compressing a foamed body of independent foams is known.

However, in the conventional method, when the foamed body of independent foams is compressed, it is necessary to cool said foamed body to the glass transition temperature or lower of the resin (for example, see Japanese Kokoku Patent No. Sho 47[1972]-31695).

The process for cooling the foamed body to the glass transition temperature or lower of the resin is complicated and industrially disadvantageous.

These inventors first variously reviewed methods for manufacturing a continuous foamed body by compressing and breaking independent foamed bodies of an ethylene polymer or ethylene copolymer, and as a result, a method that could obtain an excellent continuous foamed body by compressing and breaking independent foamed bodies even in the vicinity of normal temperature was found. Then, a method for manufacturing a continuous foamed body of an ethylene polymer or copolymer consisting of a second process that heats a compound in a first process for a fixed time, heats a crosslinked first intermediate product with a decomposition rate of 30% or less of a mixed foaming agent to a temperature higher than that of the first process, and generates a second intermediate product having easily breakable independent foams by decomposing the remaining foaming agent and crosslinking agent and a third process that breaks the independent foams by compressing the second intermediate product was invented (Japanese Patent Application No. Sho 54[1979]-76996).

According to the method of the above-mentioned invention, the crosslinked first intermediate product with a decomposition rate of 30% or less of a mixed foaming agent is obtained by heating the compound in the first process for a fixed time; however if a thick continuous foamed body is manufactured, the foam breakdown due to the compression in the third process of the second intermediate product is easy in the vicinity of the center in the thickness direction, but foam breakdown is difficult in the part near the surface. Even if the foam breakdown is easy, a nonuniform continuous foamed body with a varying foam diameter distribution is easily obtained in the vicinity of the center and the part near the surface. Thus, the conditions of the heating time and the heating temperature in the first process must be strictly controlled.

These inventors reviewed these drawbacks to overcome them, and as a result, the present invention was achieved.

In other words, the present invention is a method for manufacturing a continuous foamed body of an ethylene polymer or copolymer, consisting of a process that heats a compound in which an ethylene polymer or copolymer is mixed with a mixture of a foaming agent, a crosslinking agent with a decomposition temperature of 155°C or lower and a crosslinking agent with a decomposition temperature of 165°C or higher for a fixed time and generates a crosslinked first intermediate product with a decomposition rate of 60% or less of the mixed foaming agent; a process that heats the first intermediate product to a temperature higher than that of the first process and generates a second intermediate product having easily breakable independent foams by decomposing the remaining foaming agent and crosslinking agent; and a third process that breaks the independent foams by compressing the second intermediate product.

As the ethylene polymer or copolymer used in the present invention, there are low-density polyethylene, ethylene-vinyl acetate copolymer, ethylene-acrylic ester copolymer, ethylene-propylene copolymer, ethylene-butene copolymer, ethylene-4-methylpentene copolymer, ethylene copolymer mainly composed of ethylene, etc., and partially chlorinated polyethylene and ionomer resin are also included in them.

As the foaming agent used in the present invention, organic compounds such as azodicarbonamide, N,N'-dinitrosopentamethylenetetramine, and P,P'-oxybisbenzenesulfonyl hydrazide and inorganic compounds such as acidic sodium carbonate can be mentioned.

The amount of foaming agent used is appropriately determined in accordance with the foaming magnitude of an intended product, and the amount is generally about 2-25 parts for 100 parts resin. Thus, a product with a foaming magnitude of about 3-25 times is obtained.

The foaming agent is used with a foaming aid, so that its decomposition temperature can be regulated. As the foaming aid, urea group compounds, organic acid salt group compounds such as zinc stearate, or inorganic compounds such as basic zinc carbonate and zinc oxide can be mentioned.

As the crosslinking agent used in the present invention, there are 1,1-bis(tertiary butylperoxy) 3,3,5-trimethylcyclohexane, etc., having a decomposition temperature of 155°C or lower and dicumyl peroxide, tertiary butylcumyl peroxide, 2,5-dimethyl-2,5-di(tertiary butylperoxy)hexane, 2,5-dimethyl-2,5-di(tertiary butylperoxy)hexane-3, α,α' -bis(tertiary butylperoxy)diisopropylbenzene having a decomposition temperature of 165°C or higher.

Also, the decomposition temperature of the crosslinking agent in the present invention is indicated by the temperature for obtaining a half life of 1 min.

The amount of crosslinking agent used is appropriately about 0.5-5 parts, preferably about 0.5-3 parts for 100 parts resin. The mixture ratio of the crosslinking agent with a

decomposition temperature of 155°C or lower and the crosslinking agent with a decomposition temperature of 165°C or higher is appropriately about 1:1-70, preferably about 1:5-30.

In the method of the present invention, first, an ethylene polymer or copolymer is mixed and kneaded with a foaming agent and a crosslinking agent, and a compound with a desired shape is molded by an ordinary method. Then, said compound is put into a mold that can seal said compound, heated for a fixed time, and the foaming agent is decomposed and crosslinked.

Thus, in the first process, a crosslinked first intermediate product in which the decomposition rate of the foaming agent is 60% or less, preferably 40% or less is generated.

Here, if the decomposition rate of the foaming agent exceeds 60%, the breakdown of independent foams is difficult in the third process, though the reason for this is not certain, or a good continuous foamed body with excellent water absorption cannot be obtained. It is necessary for the first intermediate product to be crosslinked.

The degree of crosslinking can be selected in a wide range of a low degree to a high degree. The limit of the low degree is the degree that the product can be drawn out of the mold without a large deformation at the heating temperature of the first process.

The range of the degree of crosslinking is 1-95 wt% (when a 0.3 g sample is put into a wire-netted case of 200 mesh and immersed for 6 h in 100 cc xylene at 80°C, the ratio of the sample remaining in the case to the amount being charged is indicated) as a gel fraction.

The first intermediate product drawn out of the mold of the first process is heated at normal pressure or at a pressure near it in a non-airtight mold with a desired size, though it can be sealed, and the remaining foaming agent and crosslinking agent are decomposed.

The second intermediate product generated by the second process of the present invention is an independent foamed body, but the thickness of the foam wall is nonuniform. It has a structure that can change to a continuous foamed body by being compressed and broken.

The second intermediate product crosslinked and foamed in the second process is cooled to the vicinity of normal temperature and drawn out. The foaming magnitude of the second intermediate product is appropriately about 3-25 times.

For the second intermediate product drawn out of the mold of the second process, the independent foams are broken down by compressing at a normal temperature of about 0-40°C, so that a continuous foamed body is generated.

The compression may be a press or a roll press on a flat plate.

A secondary machining such as cutting of the continuous foamed body obtained through the third process into a desired shape is applied.

The continuous foamed body of an ethylene polymer or copolymer is still not on the market since the cost is high in the conventional method.

According to the method of the present invention, manufacture at a relatively low cost can be realized, and industrialization is also easy.

The continuous foamed body of the ethylene polymer or copolymer has air permeability and water absorption, compared with a conventional independent foamed body. Also, compared with a conventional polyurethane continuous foamed body, the tear strength is large, and discoloration is difficult.

The continuous foamed body of the ethylene polymer or copolymer obtained by the method of the present invention has a wide range of usage, for example, cosmetic products (puff, pad, manicure pencil tip, etc.), daily home products (scrubbing brush for cooking, window cleaner, scrubbing brush for toilet and bathtub, cushion material of bed or pillow, suit brush, coater of shoe cream, bath brush, etc.), medical equipment (cushion material in plaster cast, coater of liquid shoulder stiffness material, base material of spreading preparation or pain relief rub, etc.), industrial goods (automobile goods: packing, cushions, air conditioner filters, sound absorbing material; weak electric goods: cold insulation of refrigerator, packing, cushion of speaker, cap of microphone, etc.; city water goods: cold and heat insulation, filters, etc.; vehicle goods: door packing, etc.), business goods (stamp base, stamp, pencil tip, sponge finger tip moistening pad, printing roll, etc.), sports goods (protector, supporter, mat, mitt, cushion material of gloves, etc.), clothing goods (core of wind breaker, etc.), baby goods (core of diaper cover, cushion of vehicles, cleaner for children, etc.), shoe goods (intermediate sole of shoe, etc.), horticultural goods (water retainer put into the bottom of a plant pot, etc.), and packing goods (buffers, etc.).

Next, the present invention is explained by application examples, however the present invention is not limited to them.

Application Example 1

75 parts ethylene-vinyl acetate copolymer (trade name: Epatet D2021, 10 wt% vinyl acetate content, made by Sumitomo Chemical Co., Ltd.), 25 parts ethylene- α -olefin copolymer group elastomer (trade name: Tafmer A, made by Mitsui Petrochemical Industries, Ltd.), 12 parts azodicarbonamide group foaming agent (trade name: Vinyhole AC-3M, decomposition temperature of 200°C, made by Nagakazu Kasei Kogyo K.K.), 0.5 part zinc oxide (foaming aid), 0.5 part urea group aid (foaming aid), 0.3 part 1,1-bis(tertiary butylperoxy)-3,3,5-trimethylcyclohexane (crosslinking agent, trade name: Perhexa 3M-40 (purity 40%), decomposition temperature of 148°C, made by Nippon Oil and Fats Co., Ltd.), 1.3 parts dicumyl peroxide (crosslinking agent, decomposition temperature of 171°C), 1.5 parts liquid paraffin (agent to prevent atmospheric dispersion of foaming agent), 0.8 part stearic acid (lubricant), and 10 parts calcium carbonate (filler) were kneaded by an open roll at 70-100°C, so that a

compound was formed. Compound of about the same size was put into a rectangular mold with a thickness of 16 cm and each side of 21 cm and pressurized and heated at 130°C for a prescribed time, so that a first intermediate product was obtained.

Next, the first intermediate product was put into a rectangular mold with a thickness of 8 cm and each side of 40 cm, heated at 200-205°C for a prescribed time, and cooled to room temperature, so that a second intermediate product was obtained.

Next, the second intermediate product was passed through a roll press (a gap of 0.5-1 cm, 5 steps) at room temperature (25°C), so that a good continuous foamed body was obtained.

These results are shown in Table 1.

Table 1

| ① 実験 No. | ② 第一工程 | | ③ 第一中間製品 | | ④ 第二工程 | | ⑤ 第二中間製品の発泡倍率 (倍) | ⑥ 最終製品の連続気泡率 (%) |
|----------------|--------------|-------------|-------------|-----------------|--------------|-------------|----------------------|---------------------|
| | ⑦ 温度 (°C) | ⑧ 時間 (分) | ⑨ ゲル (%) | ⑩ 発泡剤分解率 (%) | ⑦ 温度 (°C) | ⑧ 時間 (分) | | |
| 1 | 130 | 23 | 74.5 | 23 | 200~205 | 30 | 1.8 | 100 |
| 2 | " | 25 | 78.8 | 31 | " | " | " | 95 |
| 3 | " | 30 | 83.1 | 50 | " | " | " | 80 |

(Note) 1. For the continuous porosity, the true volume of a foamed body was measured by an air comparison type gravimeter, type 930, made by Toshiba Packman Ltd., and the continuous porosity was calculated using the following expression.

$$(V_s - \Delta V) / V_s \times 100 (\text{vol}\%)$$

V_s : Apparent volume of specimen

ΔV : True volume of specimen

(Note) 2. Decomposition rate of foaming agent

Amount of gas generated by decomposing at a fixed temperature and time / generation of gas generated by a complete decomposition x 100(%)

- Key:
- 1 Experiment No.
 - 2 First process
 - 3 First intermediate product
 - 4 Second process
 - 5 Foaming magnitude of second intermediate product (times)
 - 6 Continuous porosity of final product (%)
 - 7 Temperature (°C)
 - 8 Time (min)
 - 9 Gel (%)
 - 10 Foaming agent decomposition rate (%)

Comparative Example 1

An experiment was carried out under the same conditions in the method of Experiment No. 1 of Application Example 1 except for changing the heating temperature to 140°C and the heating time to 30 min in the first process and 13 parts azodicarbonamide group foaming agent (trade name: Vinyhole DW-6, decomposition temperature of 160°C, made by Nagakazu Kasei Kogyo K.K.), 1.4 parts dicumyl peroxide, 0.8 part stearic acid (lubricant), and 10 parts calcium carbonate (filler) (Vinyhole AC-3M; zinc oxide, urea group aid, 1,1-bis(tertiary butylperoxy) 3,3,5-trimethylcyclohexane, and flow paraffin were not added) were included in the mixture preparation without changing the pattern of the ethylene-vinyl acetate copolymer and the ethylene- α -olefin copolymer.

As a result, a second intermediate product with a structure that was easily changed to a continuous foamed body by being compressed and broken down at normal temperature was obtained, and a continuous foamed body was obtained by a roll press in the third process. However, voids (an elliptic shape with a height of about 0.4 cm and a length of 1.5-2.5 cm) were generated by gas residing in the central part in the thickness direction in the vicinity of the four corners of the second intermediate product. Also, in the cross section of the foamed body, coarse foam was formed in the vicinity of the center, and fine foam was formed in the part near the surface, so that the distribution of the foam diameter was nonuniform.

On the other hand, in a single mixture of 1,1-bis(tertiary butylperoxy) 3,3,5-trimethylcyclohexane as the crosslinking agent, a difference was easily produced through the first process in the foam structure in the vicinity of the center in the thickness direction and the part near the surface in the second process for obtaining a foam structure in which the foams could be easily broken down by compressing at normal temperature, and it was necessary to very strictly control the heating condition in the first process to obtain a continuous foamed body.

Comparative Example 2

An experiment was carried out under the same conditions in the method of Experiment No. 3 of Application Example 1 except for not adding the 1,1-bis(tertiary butylperoxy) 3,3,5-trimethylcyclohexane and except for changing the calcium hydroxide (crosslinking aid) to 0.4 part.

As a result, a second intermediate product with a structure that was easily changed to a continuous foamed body by being compressed and broken down at normal temperature was obtained, and a continuous foamed body was obtained by a roll press in the third process. However, in the cross section of the foamed body, coarse foams were formed in the vicinity of

the center, and fine foams were formed in the part near the surface, so that the distribution of the foam diameter was nonuniform.

Comparative Example 3

An experiment was carried out under the same conditions in the experimental method of Comparative Example 2 except for changing the heating temperature in the first process to 140°C.

As a result, in the obtained foamed body, about 2/3 in the vicinity of the center was a continuous foamed body in the cross section of the foamed body, but about 1/3 outside the center area was an independent foamed body, and a continuous foamed body was not obtained.